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THE CORROSION OF BRASS IN DILUTE  
ELECTROLYTES

BY

BERTRAM FEUER

B. S. University of Illinois, 1919

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THESIS

Submitted in Partial Fulfillment of the Requirements for the  
Degree of  
MASTER OF SCIENCE  
IN CHEMISTRY

IN  
THE GRADUATE SCHOOL  
OF THE  
UNIVERSITY OF ILLINOIS  
1920



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UNIVERSITY OF ILLINOIS  
THE GRADUATE SCHOOL

January 17 1920.

I HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER MY  
SUPERVISION BY Bertram Feuer  
ENTITLED THE CORROSION OF BRASS IN DILUTE ELECTROLYTES.

BE ACCEPTED AS FULFILLING THIS PART OF THE REQUIREMENTS FOR  
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## The Corrosion of Brass in Dilute Electrolytes.

### I. Introduction.

In the State of Illinois certain waters are so corrosive to brass that the train of gears in water meters are eaten away in surprisingly short time. A similar occurrence has been described and studied by Monfort<sup>(20)</sup> regarding the action of St. Louis water. Because of this meter trouble the present investigation was suggested, and has led to limiting the experimental work to such ions as ordinarily occur in natural waters.

The phenomenon of rusting has been observed and noted for many years, but it is only comparatively recently that systematic investigation of the various factors that go to make up the process has been attempted. Chemically, the product of the rusting of iron is of very complex and variable composition, consisting of hydrated oxides of iron, basic ferric carbonate, and frequently sulphides, phosphates, and silicates. Rusting in a broader sense is spoken of as corrosion, a term which may be applied to the rusting of any metal, or alloy.

The greater part of the investigation in this field has dealt with the corrosion of iron and numerous theories have been advanced to explain its mechanism. These theories are usually applied to the general subject of corrosion and it is proposed in this contribution to apply them to the study of the copper-alloys.

At the present date the electrolytic theory advanced by Cushman,<sup>(7)</sup>  
(23) (27) (10) (21)  
Walker, Whitney, Fuller, and Tilden, is the most probable. We may regard all metals as exhibiting definite tendencies to go into solution





even in pure water. The magnitude of this "solution tendency" depends on two factors (I) the nature of the metal--zinc, for example possesses a very high, and platinum a very low solution-tendency, and (II) the composition of the solvent, e.g. copper possesses a high solution-tendency in ammoniacal solutions and a low one in copper sulphate. During the process of solution the metal becomes electrically charged, and the dissolved portion (in the form of hydrated metallic ions) takes on an equal and opposite charge. An electrical balance is soon reached and solution ceases unless there is some extraneous mechanism which prevents equilibrium being attained. This disturbance of equilibrium may be accomplished by the formation of numerous minute electrolytic cells over the surface of the metallic plate. Each cell consists essentially of two contiguous metals of different solution-tendency immersed in the same electrolyte.

By this means a complete electrical circuit is formed, and one electrode can continue to corrode, while at the other electrode an equivalent amount of some other metal (or hydrogen) possessing a lower solution-tendency than the dissolving metal, is deposited. It will be noticed that this theory demands for the condition of corrosion (1) the presence of contiguous conducting particles or nuclei of different electrolytic solution-tendencies; (2) contact with an electrolyte.

In the case of a pure metal there are no nuclei of solution-tendencies different from the rest of the metal, and if it were not for the fact that metals possess a crystalline structure, pure iron would not rust when immersed in tap water. The matter of the rusting of pure metals is still disputed, but according to the electrolytic theory, unless the metallic crystals are similarly orientated at the surface, a minute difference in solution-tendency will be found between crystals possessing dissimilar exposed surfaces. Provided there are in the water no metals of solution-tendencies less than that of the metal



immersed, hydrogen will be liberated at the metallic surface. The film of the hydrogen formed on the surface exerts a considerable insulating action on the metal. The difference of solution-tendencies between the crystalline electrodes is rarely great enough to permit the electromotive force of the corrosion cell to rise to that critical value where hydrogen is liberated in the form of a gas; the small cell consequently becomes polarized, and corrosion ceases. Unless there is some alternative mechanism for the removal of hydrogen, corrosion will not progress. Generally atmospheric oxygen accomplishes this by direct combination with the hydrogen; the rate of combination of the two gases consequently governs the rate of corrosion unless, as has been mentioned above, another depolariser is present. In the light of this theory the cases of brasses and bronzes can be considered. The constituents of these alloys are capable of acting as the electrodes of small corrosion cells set up over the surface of the metal, hydrogen is liberated, and some depolariser permits the cell to continue working.

Along with corrosion by electrolytic means other factors, as the composition of the metal, the solution with which it is in contact, temperature, stirring, dissolved oxygen, homogeneity, contact with metals and catalytic agents, previous mechanical and thermal treatment of the metal, nature of the surface, and so forth, enter into the process and exert very important influences. The principle of isolating each influence seems the most promising method of attack for this problem and has been used in the studies that are to be reported.

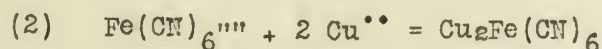
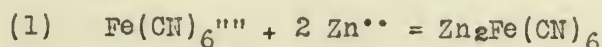
A large amount of valuable work has been done on this problem, and very noteworthy in this respect are the elaborate researches of Bengough and his collaborators<sup>(4,5)</sup> on the corrosion of brass condenser tubes by sea-water. Bengough<sup>(3)</sup> has defined two types of corrosion, "complete" and "selective". In





"complete" corrosion the components of the brass are equally corroded---that is, in the proportion in which they occur in the alloy. This form of corrosion is due to direct oxidation by dissolved oxygen. In "selective" corrosion only one ingredient (the zinc) is corroded. The action in this case is electrolytic and depends on differences of potential, either within the brass, or between the brass and some metal in contact with it. In the case of brass, zinc is usually the corroded element and its removal is called "dezincification." The characteristic of this selective form of corrosion is pitting, or even perforation. The zinc is removed leaving a matrix of the copper in a porous and weak form. The action is localized around that part of the couple which functions as the cathode, and differs conspicuously in general appearance from corrosion due to oxidation.

As a demonstration of the electrolytic theory and also for a preliminary study of several alloys, use has been made of the ferroxyl indicator described by Cushman and Walker.<sup>7</sup> The indicator was prepared with pure agar-agar and tap water, and saturated with carbon-dioxide gas before using. Polished specimens of the alloys\* listed in Table I were immersed in the jelly and kept in a carbon-dioxide atmosphere for a period of ten days. As corrosion progresses the zinc and copper ions leaving the metal react with the potassium ferrocyanide contained in the indicator, according to the following reactions:-



The product formed according to reaction (1) is a white precipitate while the product formed according to reaction (2) is reddish-brown. In this way the zinc and copper ions that have migrated from the metal to the solution are easily recognized. Plates 1a and 1b show the front and back views of the speci-

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\*Samples and analysis were obtained through courtesy of The American Brass Co.



mens at the end of ten days. The curve shown in Fig. 1 was made by approximating the areas produced by the formation of  $\text{Zn}_2\text{Fe}(\text{CN})_6$ , and plotting these values against the percentage copper content of the samples. It will be noticed that the Cu-Al alloy did not corrode, on the other hand report is made by the manufacturers of this alloy that from their tests by immersion in sea water, this alloy at the end of 40 months lost more weight than did the other alloys, given in Table I, that were exposed to the same conditions. In sea water this Cu-Al alloy lost weight as follows:

<u>4 Mo.</u>	<u>11 Mo.</u>	<u>18 Mo.</u>	<u>40 Mo.</u>
0.04%	0.6%	17.0%	36.4%



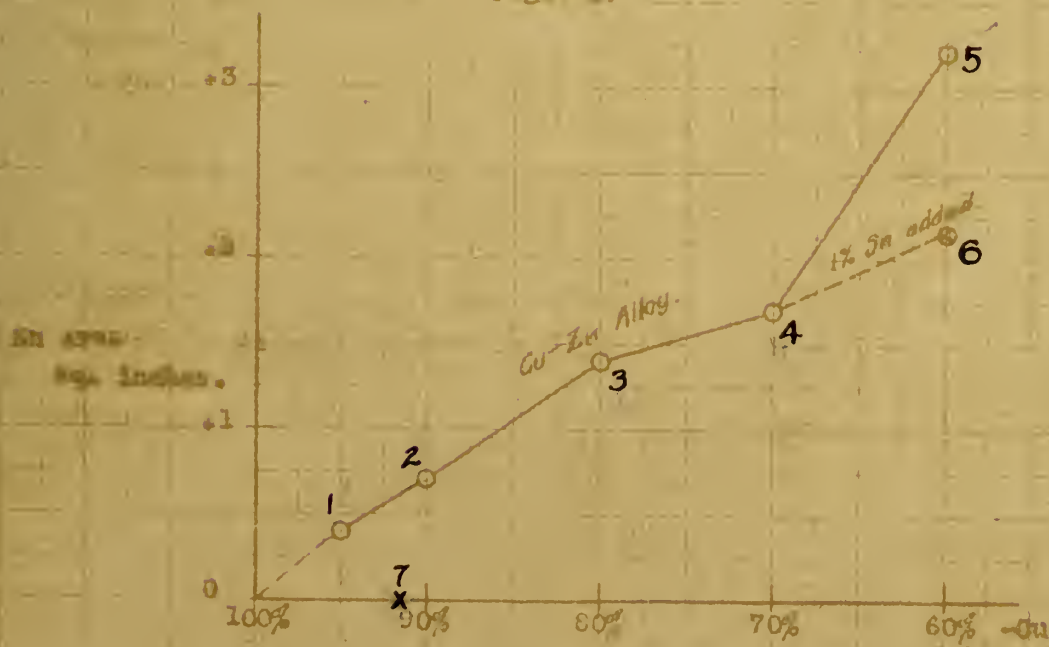


TABLE NO. 1.

After 10 days corrosion in Agar Jelly

No.	Percent Cu	Zn	Zn area produced (in sq. inches)
1	98	5	0.42
2	90	10	0.70
3	80	20	1.40
4	70	30	1.68
5	60	40	3.20
6	60	39	2.15
Sn - 1 %			
7	92		not affected
Al - 8 %			

Fig. 1.





## II. EXPERIMENTAL

Magnitude of Potential Differences--- The potential differences between pieces of bright copper and bright zinc were measured at room temperature (21-22°C.) in several solutions, obtaining initial values of 0.9-1.0 volt. (See Table II.) Assuming that there are distinct particles of copper and zinc

Table II. Potential Differences between Copper  
and Zinc

Cu : 0.1 M HCl	: Zn	.92 volt.
Cu : 0.1 M KCl	: Zn	.92 "
Cu : 0.1 M KNO <sub>3</sub>	: Zn	.92 "
Cu : 0.1 M KNO <sub>2</sub>	: Zn	.98 "
Cu : 0.1 M NH <sub>4</sub> Cl	: Zn	.95 "
Cu : 0.1 M NaHCO <sub>3</sub>	: Zn	1.04 "

present on the surface of the brass, this gives an approximate measure of the intensity factor operating at the start in the electrolytic corrosion of brass. This difference becomes smaller as corrosion proceeds, due to polarization effects; but since in practice the volume of the solution is exceedingly large and since the liquid is frequently in constant motion, the working value of this potential may remain high. This was shown in the following manner: The electrodes just referred to were short-circuited for 24 hours in a 0.1 M KCl solution, washed as thoroughly as possible in that solution, and upon remeasuring gave a potential of .76 volt. This indicated that, with an electrolyte of good conductivity, electrolytic corrosion of brass may be very considerable.

Role of the Ions--- The corrosive influence of the common ions of natural waters was investigated by observing variations of current-potential. An electrolytic cell was set up, using as an anode a piece of 80:20 brass, 2 x 2.5 cm., and as a cathode a piece of bright sheet platinum. Care was taken that the relative positions of the electrodes should be unchanged in the various





experiments, and that the stirring should be as uniform as possible. Figure 2

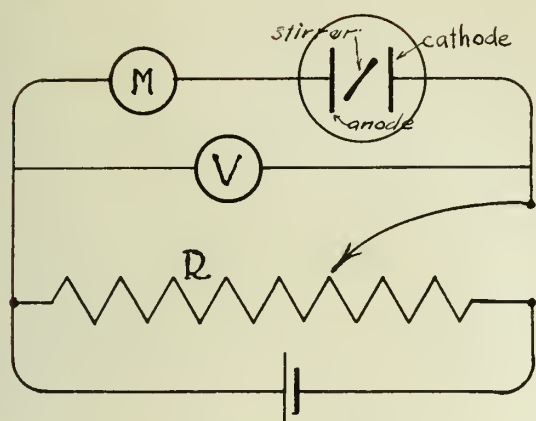


Figure 2.

shows a diagrammatic arrangement of the apparatus. Increasing potentials were applied by means of the sliding resistance  $R$ , and were read directly from the volt-meter  $V$ , which was placed on a shunt around the cell and current instruments. For the measurement of the current a milliammeter,  $M$ , was used.

The curves for 0.1 molar solutions of  $\text{KNO}_3$ ,  $\text{KCl}$  and  $\text{KHCO}_3$  are shown in Figure 3. The curves for 0.05 M  $\text{K}_2\text{SO}_4$  and 0.1 M  $\text{KNO}_2$  are almost superposable with that for 0.1 M  $\text{KNO}_3$ , and for that reason were not included in the figure. On account of the double flexure in the  $\text{KCl}$  curve it is not easy to compare the influences of these anions on corrosion. Assuming that the operative potential lies within the range 0.7-1.0 volt, it would appear that there is very little difference in the corrosive effects of  $\text{Cl}$ ,  $\text{NO}_3$ ,  $\text{NO}_2$  and  $\text{SO}_4$ -ions. The action of  $\text{HCO}_3$ -ion is, for some unexplained cause, much less than the others.

The sinuous form of the chloride curves requires an explanation. All the chloride solutions used showed decided double flexures, with the exceptions of  $\text{HCl}$  and  $\text{NH}_4\text{Cl}$ . The double flexure in current-potential curves is generally interpreted to mean a change in reaction at one of the electrodes. In the case of solutions containing  $\text{Cl}$ -ions, the anode reaction with brass electrodes at low potentials seems to be the discharge of  $\text{Cl}$ -ions forming cuprous chloride as a primary product. Owing to the insolubility of cuprous chloride, polarization effects are very slight and the current mounts rapidly with the first increase in potential. At higher potentials a second reaction begins--the direct ionization of the copper of the brass,-- and this gives a second stimulus to the current. The second flexure is in the neighborhood of a potential of 1.0 volt,



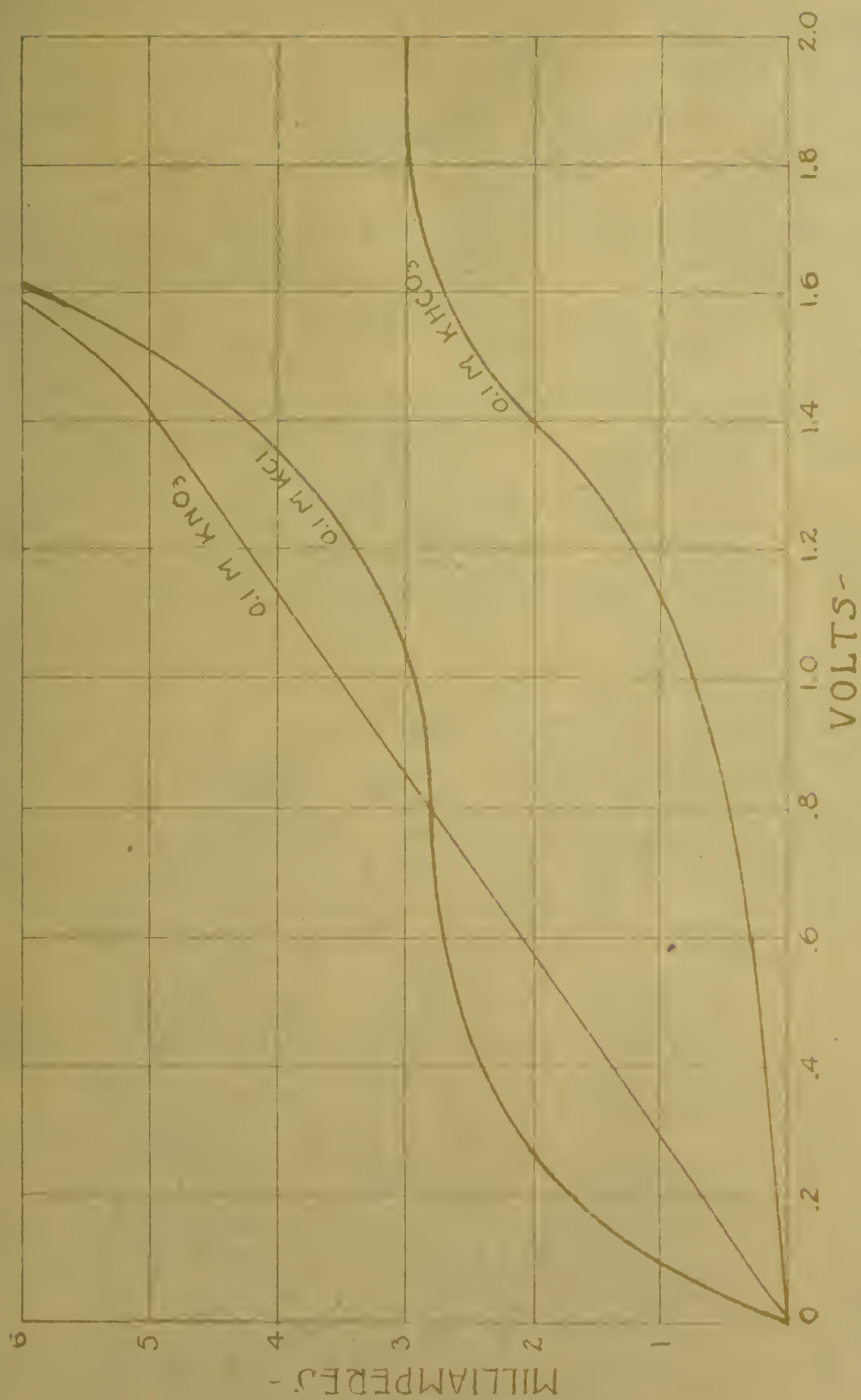


Fig. 5-- Current-voltage curves for 0.1 M KNO<sub>3</sub>, KCl, KHCO<sub>3</sub>.





its position being displaced in different solutions by different cathode potentials. In some cases, as HCl and  $\text{NH}_4\text{Cl}$ , curves of apparently different types were obtained, but the abnormality is more apparent than real. In HCl the second flexure is displaced to the left by an elevation of the cathode potential, and in  $\text{NH}_4\text{Cl}$  the first part of the curve is modified by a side reaction--the formation of  $\text{NH}_3$ -complexes.

Observations of current-potential were also taken for sets of solutions having a common anion, so as to get comparative values for the influence of several cations. (See curves Figure 4.) With HCl solution marked corrosion is indicated, as would be expected from the high mobility of the H-ion. With solutions of metallic chlorides, the corrosion is much less. This is due to the fact that the cathode reaction is the discharge of H-ions, and the amount of current passing at the cathode depends directly upon the concentration of these ions. From this it follows that solutions which are acid, either by reason of a free acid or owing to hydrolysis, are favorable mediums for corrosion.  $\text{NH}_4\text{Cl}$  and  $\text{CaCl}_2$  solutions appear more corrosive than KCl or NaCl of equivalent concentration, the difference being due to the hydrolytic formation of free HCl in the first two solutions.

The curves shown in Fig. 5 were made from data obtained by taking a series of current-potential measurements in 0.1, 0.01, and 0.001 molar solutions of  $\text{KNO}_3$ , to show the effect of concentration on electrolytic corrosion. It is significant that the current increases with the conductance of the solution, indicating that in electrolytic corrosion high concentrations (by lowering the resistance of the liquid part of the circuit) would strongly stimulate corrosion.  
11,16

It has been suggested by some writers that a solution containing two or more salts might be more corrosive than the combined effect of the component salts when taken separately. Observations of current-potential of several



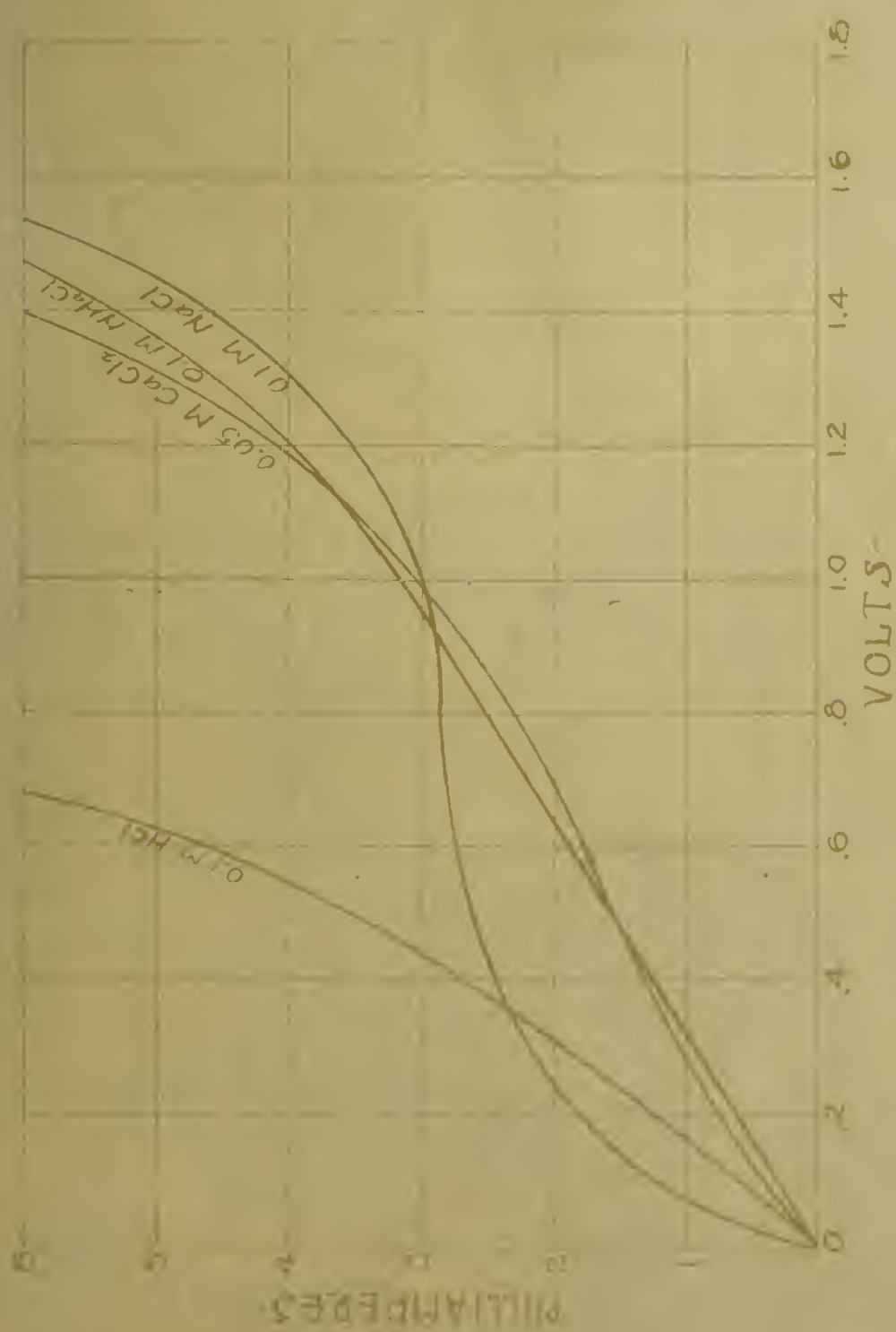
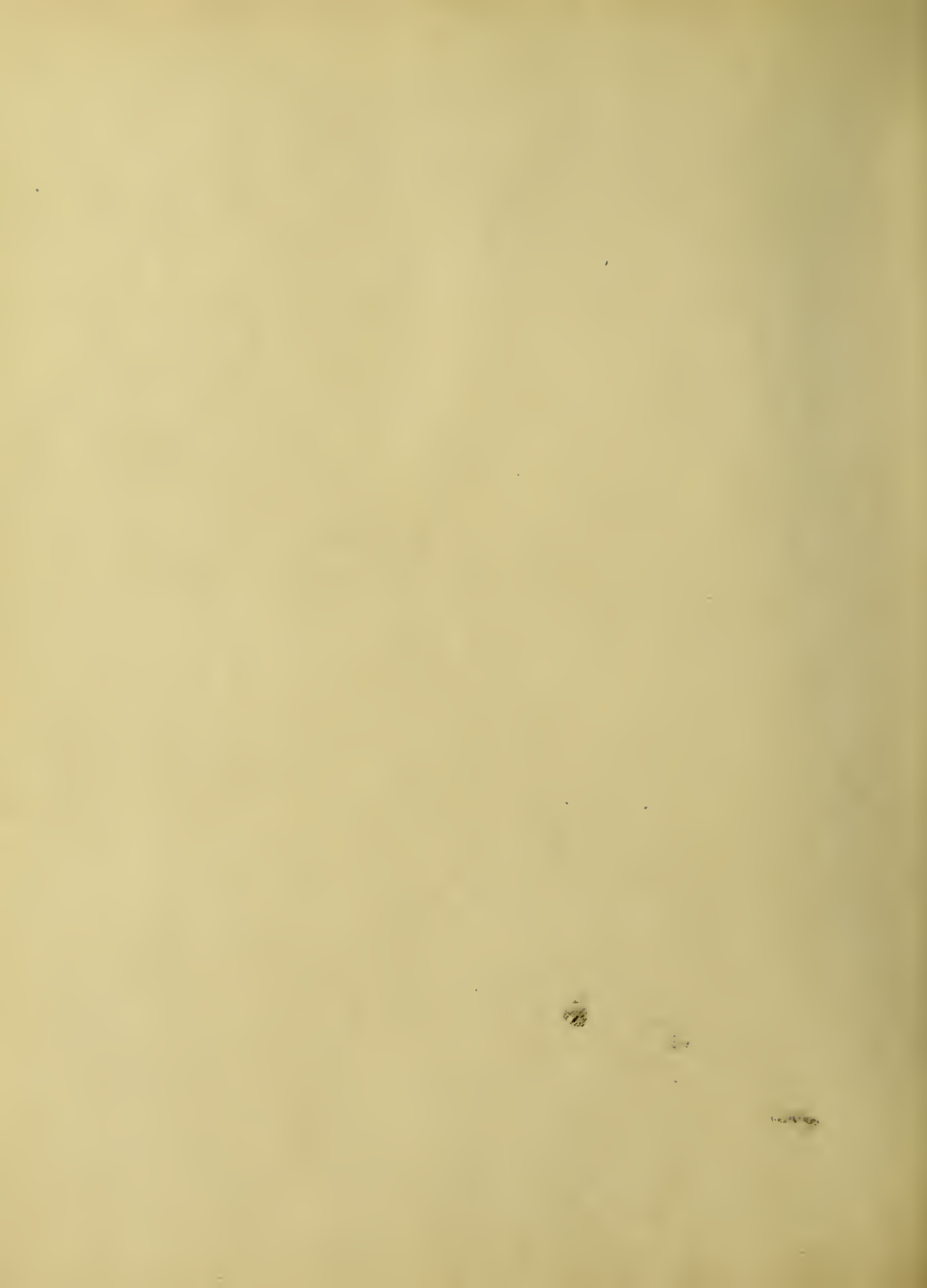


Fig. 1. Electrochemical current vs. voltage for 0.1M NaCl, 0.05M CaCl<sub>2</sub>, 0.1M HCl.





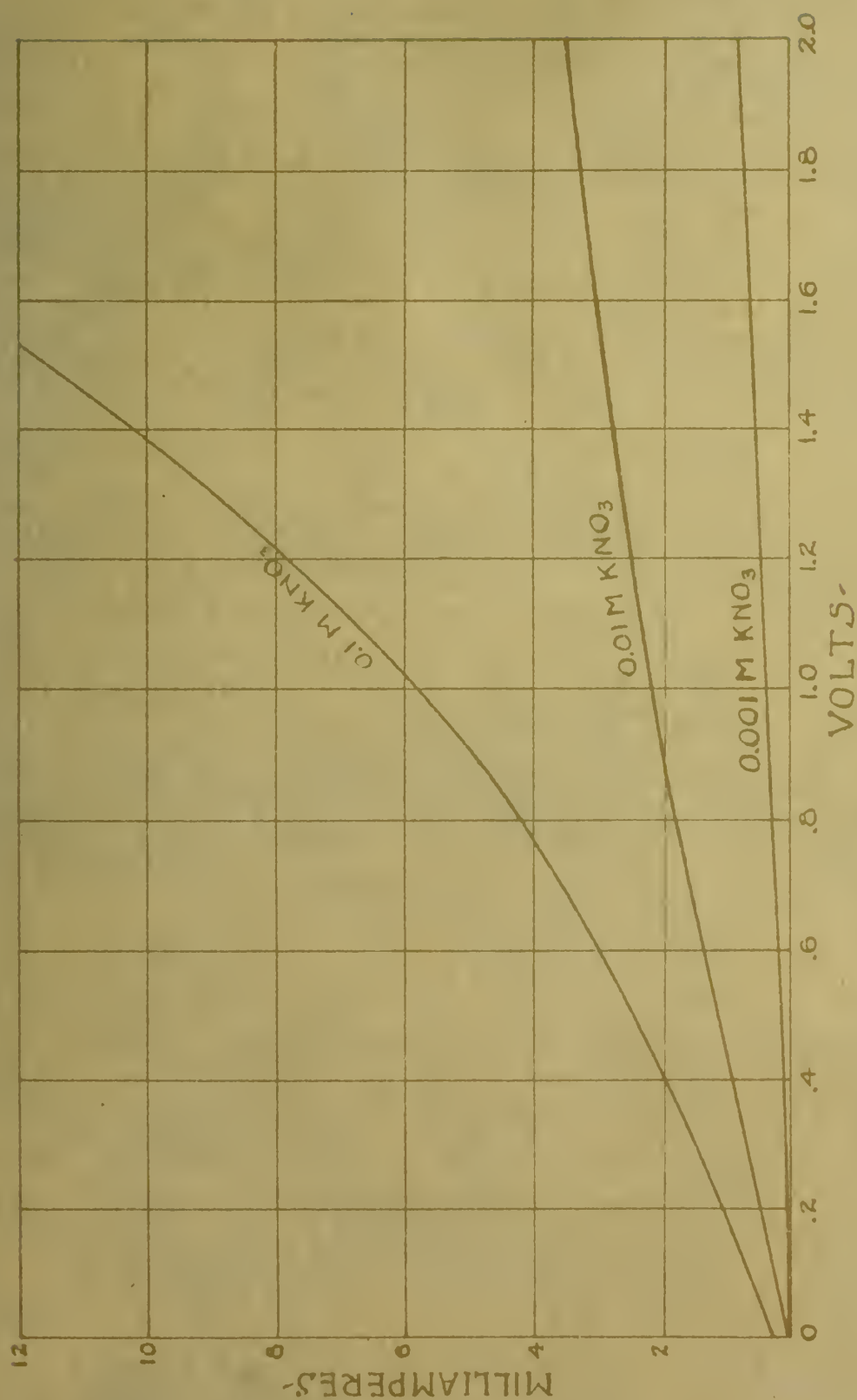


Fig. 5-- Current-potential curves for 0.1, 0.01, and 0.001 molar KNO<sub>3</sub>.



mixtures were made and the total current was found to be very nearly equal to the sum of the currents for separate solutions of single salts of equivalent concentrations to those in which they occurred in the mixture. It is inferred that the influence of the various ions on electrolytic corrosion is an additive property.

Corrosion Products-- Very naturally corrosion products vary with the electrolyte. The products for low potentials in neutral solutions are basic salts which are only loosely adherent to the anode. At higher potentials the solution becomes turbid and its color shows an increasing amount of dissolved copper. Basic copper chloride was found to be very stable, and constituted the principal part of the corrosion product with neutral chlorides. With nitrates and sulfates, basic zinc salts predominated. Solutions containing  $\text{HCO}_3^-$ -ions appeared rather non-corrosive from the electrolytic point of view, and no appreciable precipitate formed unless high potentials were impressed.

Influence of Dissolved Oxygen in Electrolytic Corrosion-- Some have assumed that dissolved oxygen would stimulate electrolytic corrosion by acting as a depolarizer at the cathode. In order to verify this assumption, observations of current-potential were made for 0.1 M  $\text{KNO}_3$ , using a brass anode and a copper cathode. In one experiment, the solution (previously boiled to expel air) was stirred by a jet of nitrogen bubbled into the solution close to the cathode. In a second run, the solution was stirred with filtered,  $\text{CO}_2$ -free air instead of nitrogen. The current-potentials observed were identical within the limits of experimental error. A solution of 0.1 M  $\text{KCl}$  gave similar results. It is concluded that dissolved oxygen is without significant effect in electrolytic corrosion.

Composition of the Brass-- The measurements cited above were made with an anode of commercial brass containing 80% copper and 20% zinc. With the aid





of an auxiliary electrode (mercurous sulphate) a series of commercial alloys of varying composition were investigated by making potential fall measurements between the surface of the metal and the solution in which it was immersed. The results obtained showed the behavior of the samples listed in Table III to be very similar and it was for this reason that the 80:20 sample was taken as representative.

Table III.

<u>Sample No.</u>	<u>% Cu</u>	<u>% Zn</u>	<u>% Sn</u>
2	90	10	-
3	80	20	-
5	60	40	-
7	60	39	1

Influence of Temperature-- At elevated temperatures the effects of electrolytic corrosion are greater and the life of brasses exposed to aerated natural waters is much shortened, owing to pitting and possible perforation. High temperatures favor corrosion in two ways, viz.: (1) The mobility of the ions is increased, thus greatly reducing the resistance of the liquid phase of the circuit; and (2) there is an acceleration in the speed of the reactions involved, such as the ionization of the zinc, and so forth.

The above experiments suggest very strongly that--so far as electrolytic corrosion is concerned--the role of most ions is immaterial, except as they maintain the conductivity of the solution. Certain ions, on the other hand, show a specific corrosive action. In the case of Cl<sup>-</sup> ions, this is connected with the removal of the ions of the anode metal by converting them into insoluble compounds or else into complexes of low ionization. In other words, they act as depolarizers. Another example, waters containing H<sub>2</sub>S are corrosive, not so much on account of their acidity, but because of the formation of insoluble ZnS



and  $\text{CuS}$ . Solutions of ammonium salts act very much in the same way, in that the solution becomes alkaline and free  $\text{NH}_3$  is formed, and this unites with Zn and Cu-ions to form  $\text{NH}_3$ -complexes of low ionization. This explains to some extent the large current with  $\text{NH}_4\text{Cl}$  solution.

Complete Corrosion-- It is easily demonstrated that fine copper is tarnished in the presence of moist air. Pure zinc is similarly coated with a layer of zinc oxide. Under similar conditions brass corrodes, but much more slowly, to a corrosion product containing copper oxide. It is clear that such reactions are not electrolytic, since in the first two cases the metals are quite homogeneous and the corrosion is general, not local. In the case of brass, electrolytic corrosion would hardly result in the solution of the nobler component copper. It appears that this form of corrosion is due to oxidation by dissolved oxygen and is known as "complete" or "general" corrosion.

Oxygen Essential to Complete Corrosion-- In corrosion, either hydrogen must be liberated, or oxygen (or some chemically analogous substance) must be taken up from the air or another oxidizing agent. In order to learn whether hydrogen was liberated in brass corrosion, pieces of soft brass,  $1.5 \times 7$  cm., were placed in 0.1 M solutions of  $\text{HCl}$ ,  $\text{KCl}$ ,  $\text{NH}_4\text{Cl}$ , and  $\text{NH}_4\text{NO}_3$ , each of which had been boiled to expel absorbed oxygen. The apparatus consisted of 20 cc. glass-stoppered weighing bottles, each of which, after introducing the brass, was completely filled with the solution so as to exclude all bubbles. Each bottle was then placed in a cylinder and covered with an excess of the same solution that it already contained, so as to seal it from access of air by leakage. After standing for somewhat different lengths of time (see Table IV), the brass remained bright, and no bubbles of gas appeared in any of the tubes, indicating that no hydrogen was evolved. With 6 M  $\text{HCl}$  (specific gravity = 1.12) brass was likewise inactive at ordinary temperatures. Upon heating, at temperatures





Table IV.

Effect of Absence of Dissolved Oxygen on Complete Corrosion.

<u>Solution</u>	<u>Air Dissolved</u>	<u>Length of Test</u>	<u>Loss in Weight</u>
0.1 M KCl	Saturated by frequent shaking	37 days	.0125 gram
0.1 M KCl	None	37 "	.0010 "
0.1 M HCl	"	26 "	.0012 "
0.1 M NH <sub>4</sub> Cl	"	26 "	.0003 "
0.1 M NH <sub>4</sub> NO <sub>3</sub>	"	24 "	.0006 "
6 M HCl	"	17 "	.0010 "

slightly below 50°, evolution of hydrogen began. The above table shows, that while there was no visible liberation of gas, there was a certain amount of corrosion in all cases, the amount, however, being small in comparison with that occurring when air was present.

Hence, it is concluded that oxygen is necessary to extensive corrosion of brass in dilute solutions at ordinary temperatures. Similar results were<sup>1</sup> obtained by Adie in his studies of iron in 1845, and have since been fully confirmed by the very careful investigations of Friend.<sup>9</sup>

Measure of Corrosion--Various methods have been used in determining the amount of corrosion. The oldest method which is still used by a number of investigators is the immersion test. Strips of metal are carefully cleaned and weighed, and are placed in samples of water. After the lapse of a certain period of time the samples are removed, carefully cleaned with either a brush or rubber-tipped rod, dried, and weighed. The loss in weight is determined and considered the measure of corrosion. Acceleration tests, such as in 20% sul-<sup>3</sup>phuric acid, in 7.5% sodium chloride, or in 1 % ammonium nitrate solutions<sup>25</sup> have been proposed and attempted. G. and M. Whipple introduced an electrolytic test for corrosion in which the rate of solution was accelerated by making the test piece of the metal the anode of a cell driven by current from some external source. Another electrolytic test devised by H. Hansen and W. Lewis<sup>15</sup> for de-



termining the mutual corrosive effect of two metals consists in connecting electrodes of two metals through an ammeter, keeping the solution about the electro-negative metal saturated with air, and measuring the current in the external circuit.

A very promising method which has only had preliminary investigation is that mentioned in the section on "Composition of the Brass." In the present work immersion tests were investigated. It was found that they can be made more accurate by removing the deposits chemically. The corroded test piece is immersed in cold HCl of sp.gr. 1.12 for one minute, rinsed thoroughly with distilled water which has been boiled to expel air, and dried between filter papers. In a series of four blank tests, using brass pieces 2.5 x 6.5 cm., the average loss on this treatment was 0.00035 grams. Ammoniacal and alkaline cyanide solutions were also tried as solvents for the corrosion products but were discarded because of poor efficiency and marked tendency toward oxide formation in the subsequent rinsing.

The data obtained from some of the tests is given in Table V, (see also Plate III). These tests were made on pieces of 80:20 brass, 2.0 x 0.75 in., suspended from glass hooks. The pieces entirely immersed suffered primarily from electrolytic corrosion, while those only partially immersed were under the influence of oxidation. It is interesting to note that the sample entirely immersed in the  $\text{KNO}_2$  solution lost no weight. On the other hand, it was observed that after the second trial minute "pits" were formed on the surface. No doubt that if this piece were left in contact with the solution for a longer period of time corrosion would have progressed rapidly, in the form of pitting.

Another very promising means of determining corrosion depends upon oxygen consumed as an index of corrosion. Pieces of brass of convenient size were placed in small tubes connected with mercury manometers of the open arm type.





The solution to be used was shaken with air at room temperature until saturated, and a definite volume introduced. The tube is best closed by sealing off the capillary end of a vent tube, so as not to disturb the level of the mercury in the manometer. This method affords a means of learning not only the relative corrodibility of two or more specimens of brass, but gives the needed information about the speeds of corrosion. Owing to the fact that rubber stoppers were used, the results were vitiated in most of the experiments either through leakages around the tubes or diffusion through the rubber. Ground glass joints seem to be required.

Table V.

Solution tenth-normal	Loss in wt. after 30 days.	2nd Trial
*KCl	.0245	.0285
°KCl	.0180	.0210
*K <sub>2</sub> SO <sub>4</sub>	.0045	.0030
°K <sub>2</sub> SO <sub>4</sub>	.0025	.0045
*KNO <sub>3</sub>	.0025	.0035
°KNO <sub>3</sub>	.0020	.0030
*KNO <sub>2</sub>	.0015	.0185
°KNO <sub>2</sub>	.0000	.0000
*MgSO <sub>4</sub>	.0030	.0030
°MgSO <sub>4</sub>	.0030	.0025
*MgCl <sub>2</sub>	.0170	.0130
°MgCl <sub>2</sub>	.0175	.0180

\*Sample half immersed

°Sample entirely immersed

6,11,16,18

Influence of Ions on Complete Corrosion-- Many observers have reported that there are wide differences in the corrosive action of various solutions. The specific influence of various solutions was determined by the present investigators in the following way: Pieces of soft brass, 2.5 x 6.5 cm., were placed in 150 cc. glass-stoppered bottles and covered with 100 cc. of the solution to be investigated. The bottles were thoroughly shaken so as to





saturate the solutions with air, and the shaking was repeated every 24 hours. These tests were carried out in groups of eighteen, and every care was taken to make the conditions as uniform as possible. After standing 15 days, the pieces were removed, cleaned in HCl solution of 1.12 gravity as previously described, and the loss in weight determined. Table VI gives the results obtained.

Table VI.

Comparison of Complete Corrosion in Various Solutions.

<u>Solution</u>	<u>Loss in Wt.</u>	<u>Remarks</u>
Distilled H <sub>2</sub> O	.0016 gm.	Brownish-red tarnish.
0.1 M HCl	.0744	No stain. Cu-plate on edge.
0.1 M KCl	.0105	Local red stains. Slight precipitate containing Zn, Cu.
0.1 M NaCl	.0033	Local red stains. Slight precipitate containing Zn, Cu.
0.1 M NH <sub>4</sub> Cl	.0721	No tarnish. Colorless solution. Blue precipitate containing Cu only.
0.05 M CaCl <sub>2</sub>	.0151	Slight reddish stain. Precipitate containing Zn, Cu.
0.05 M CaCl <sub>2</sub>	.0166	Slight reddish stain. Precipitate containing Zn, Cu.
0.1 M KNO <sub>3</sub>	.0032	Local black splotches. Traces of NH <sub>4</sub> <sup>+</sup> and NO <sub>2</sub> <sup>-</sup> in solution.
0.05 M K <sub>2</sub> SO <sub>4</sub>	.0044	General tarnish. Local black stains. Trace of sulfide in corrosion product.
0.1 M KNO <sub>2</sub>	.0017	Local black stains.
0.1 M NH <sub>4</sub> NO <sub>3</sub>	.1120	General black tarnish. Colorless solution. Precipitate containing Cu, Zn.
0.1 M NaHCO <sub>3</sub>	.0155	General darkening, with local red stains.
0.1 M KHCO <sub>3</sub>	.0249	General darkening, with local red stains.
1.0 M KCl	.0058	Bright. Slight precipitate containing Cu.
0.01 M KCl	.0092	Covered with red-brown stain.
1.0 M NH <sub>4</sub> Cl	.3306	Bright. Blue solution. Green precipitate containing Cu.
0.01 M NH <sub>4</sub> Cl	.0294	Red-brown stain. Blue solution. Greenish precipitate containing Cu, Zn.



Comparative values of the influence of various anions may be obtained from a consideration of the 0.1 M potassium salts in the above table. They fall into the following order (the most corrosive first):  $\text{HCO}_3^-$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{--}$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{OH}^-$ . The order of the cations is:  $\text{H}^+$ ,  $\text{NH}_4^+$ ,  $\text{Mg}^{++}$ ,  $\text{Ca}^{++}$ ,  $\text{K}^+$ ,  $\text{Na}^+$ .

The  $\text{HCO}_3^-$ -ions were the first to show visible action. In 5-6 hours the test pieces were almost wholly covered with a black deposit of what seemed to be  $\text{CuO}$  containing carbonates. The deposit seemed to exert little protection for the uncorroded brass, as is indicated by the high corrosion.

Marked corrosion has always been found in solutions containing chlorides. Their specific action seems to be directly related to two things, viz.: (1) The insolubility of the basic chlorides of zinc and copper, and (2) their marked power for dissolving oxygen. A characteristic of the corrosion by neutral chlorides is the formation of brownish splotches which appear to be regions of pure copper, and not of cuprous oxide, as some workers have reported. This conclusion is based upon the insolubility of these stains in dilute  $\text{HCl}$  and in  $\text{KCN}$  solutions. Another interesting observation is what is apparently copper plating of the brass. The deposit has exactly the same appearance as the deposit formed upon placing brass in a solution of  $\text{CuCl}_2$ . It is suggested that the copper first goes into solution by general corrosion, and is later precipitated by the zinc of the brass. This phenomenon was noticed only in chloride solutions.

Sulfates are characterized by a general darkening of the brass, and later by the formation of dark splotches. On the fourth day a slight precipitate of what was taken to be basic zinc sulfate appeared. A trace of  $\text{CuS}$  was formed during the corrosion; the amount seemed too small to account for the total corrosion loss. It is thought that the main action is direct oxidation, rather than the reduction of sulfate to sulfide.





In nitrate solutions brass might be expected to behave as a zinc-copper couple, reducing the nitrate readily to ammonia. Here, as in other ways, there is a sharp contrast between brass and its constituents in the form of a couple. In the 0.1 M  $\text{KNO}_3$  solution the brass piece seemed almost inert. With the exceptions of dark stains localized on some scorings formed in rolling the brass, the piece remained bright. At the end of the 15-day period of corrosion, Nessler's reagent and the  $\alpha$ -naphthylamine-sulfanilic acid reagent showed the presence of small amounts of  $\text{NH}_4^+$  and  $\text{NO}_2^-$ , respectively. Nitrites are even less corrosive than nitrates.

The corrosive influence of the cations has already been forecasted. The action of free acids--that is, solutions containing the H-ion--consists in dissolving oxides just as fast as they form. Again, if the free acid has a specific oxidizing influence, like  $\text{HNO}_3$ , its corrosive effect will be accordingly intensified. Formation of free acids hydrolytically, as  $\text{HCl}$  from  $\text{MgCl}_2$  and  $\text{HNO}_3$  from  $\text{NH}_4\text{NO}_3$ , explains the marked increase of the corrosive action of these solutions beyond that of  $\text{KCl}$  and  $\text{KNO}_3$ . The  $\text{NH}_4^+$ -group has an exceedingly corrosive effect by reason of the formation of  $\text{NH}_3$ -complexes. These very simple and natural assumptions are sufficient to explain the intensified activity of  $\text{MgCl}_2$ ,  $\text{CaCl}_2$ , and  $\text{NH}_4\text{NO}_3$ . Tests with litmus paper showed a development of alkalinity in all the neutral salt solutions used.

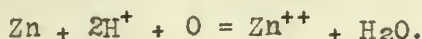
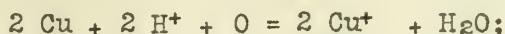
Influence of Dissolved Oxygen on Complete Corrosion-- Undoubtedly a contributory influence in general corrosion is the solubility of oxygen in the various solutions. <sup>2,8,26</sup> Oxygen is more soluble in an acid than in one of its salts of the same concentration, and more soluble in a salt than in the corresponding base of the same concentration. <sup>12.</sup> Furthermore, solubility diminishes with increase in concentration. For this reason (see 1.0 M  $\text{KCl}$ , 0.1 M  $\text{KCl}$  and 0.01 M  $\text{KCl}$  in Table VI) corrosion falls off at higher concentrations, and a





high enough concentration may completely inhibit it. Such limiting values of concentration have been defined in the corrosion of iron. The divergence of acids and ammonium salts from this behavior may be inferred from what was stated above.

Mechanism of Complete Corrosion-- As a working hypothesis the following are assumed to be the fundamental reactions in complete corrosion by dissolved oxygen:



The equilibrium may be shifted in the forward direction in three ways: (1) Increase in the concentration of H-ions-- that is, the acidity; (2) increase in the concentration of the dissolved oxygen, which varies with different solutions; (3) removal of the Cu and Zn-ions by (a) precipitation as oxides or other insoluble substances, (b) complex ion formation, as  $\text{Cu}(\text{NH}_4)_2^+$  and  $\text{Zn}(\text{NH}_4)_4^{++}$ , and (c) oxidation of  $\text{Cu}^+$  to  $\text{Cu}^{++}$ .

This conception of an equilibrium gives a ready explanation of several of the outstanding features of brass corrosion. The well-known fact that alkalies of moderate concentration inhibit corrosion follows from the repression of the H-ion. The so-called catalysis by means of dissolved  $\text{CO}_2$  is explained not so much by the slight increment of H-ions as by the removal of Cu and Zn ions by the  $\text{HCO}_3$ -ion. Those solutions which are the best solvents for oxygen are generally the most corrosive.

Other Significant Influences-- The effect of stirring on the speed of corrosion is well known and needs no discussion. Contact action is one of the most important factors in corrosion, but the writers have not been able to include this problem in the present investigation. An illustrative case is in one of the manometer experiments where a piece of brass stood in contact with a solu-



tion for several weeks with no sign of corrosion; but when once a splotch of black cupric oxide appeared at one point corrosion proceeded rapidly and the stain at once spread over the whole test piece. This behavior has its analogue in the rusting of iron and steel, where the hydrated oxide catalyzes rust formation to a marked degree.<sup>9</sup> Contact with metals nobler than copper strongly catalyzes the corrosion of brass.

The nature of the surface seems of significance. Pieces of brass which have been etched chemically corrode more rapidly than mechanically polished ones. This may be partly due to increase in surface. Usually corrosion begins at an edge of the test piece, indicating that the strained condition caused by the cutting leaves the edges in a more reactive form. In a few cases corrosion started on the scorings left in rolling the sheet brass at the mill. This behavior is comparable to that of steels,<sup>13</sup> where strains in the metal seem to affect its corrodibility to a noticeable extent.





### SUMMARY

The experiments described above point very decidedly to the conclusion that there are two kinds of brass corrosion, viz.: Electrolytic and Complete.

The specific influences of various factors in corrosion may be summarized as follows:

- (1) High concentration of electrolytes favors electrolytic corrosion in an additive way, and retards, or even inhibits, complete corrosion.
- (2) Elevated temperatures favor electrolytic corrosion, but diminish complete corrosion by reduction of dissolved oxygen.
- (3) Contact with metals nobler than brass favors electrolytic corrosion, and is without influence on complete corrosion.
- (4) Dissolved oxygen has no appreciable effect on electrolytic corrosion, but is essential to complete corrosion.
- (5) The presence of ions or groups that combine with Zn and Cu-ions to form compounds of low ionization favors both electrolytic and complete corrosion.
- (6) There is no specific influence of ions in electrolytic corrosion except in the case of ions that form complexes of low ionization and in the case of H-ion; on the other hand there is marked specificity in complete corrosion, believed to be largely determined by oxygen solubility.
- (7) Homogeneity reduces electrolytic corrosion, and has no effect on complete corrosion.
- (8) Other influences are operative--catalysis, nature of surface, strained areas in the alloy, etc.-- but they have not been included in this investigation.

It is doubtful whether in practice either form of corrosion ever





occurs to the exclusion of the other. In complete corrosion, dezincification occurs as a secondary process by the displacement of copper from the solution; and since electrolytic corrosion usually takes place in contact with the air, primary oxidation of the alloy is possible.



### III. Appendix.

In the consideration of oxidation in the process of corrosion by a mineral water, there are as possible sources of oxygen; atmospheric oxygen, dissolved oxygen,  $\text{SO}_4$ ,  $\text{NO}_2$ , or  $\text{NO}_3$ -ions. In the latter cases it is obvious that these  $\text{SO}_4$ ,  $\text{NO}_2$ , or  $\text{NO}_3$  ions must be reduced to release the oxygen. It is well known that iron will reduce nitrates to ammonia very readily. In a similar way it should be possible for brass to reduce, and it is the object of this part to demonstrate the same.

#### Reduction of Nitrates.

##### Section A. (at room temperature)

Brass strips (9 x 1/2 inches) were cut from one large sheet of common yellow brass. The strips after being thoroughly cleaned and polished were set in 50 cc. "Nessler" tubes together with 50 cc. of  $\text{KNO}_3$  solution of varying concentrations. The concentrations of the  $\text{KNO}_3$  in the tubes, expressed in p.p.m. of nitrate-nitrogen are given in Appendix, Table I. These tubes were stoppered and left in an upright position for a period of 30 days, at room temperature, after which time the contents were removed and analyzed for their nitrate-nitrogen content. This was repeated in a similar way using fresh solutions of  $\text{KNO}_3$  and the same strips of brass. The strips used in the second trial were not repolished, merely washed and dried. The results, together with complete data, are given in Table 1. A graphical representation of the results will be found in Appendix, Figure 1.

A rather white flocculent precipitate was observed in all the tubes. The





abundance of the precipitate which settled to the bottom was distinctively in proportion to the increasing concentrations of the  $\text{KNO}_3$ . Examination of the brass strips showed that the amount of corrosion was approximately proportional to the concentration of the  $\text{KNO}_3$ . A qualitative test showed the presence of increasing amounts of zinc, reaching a maximum concentration in the tube containing the largest amount of  $\text{KNO}_3$  solution.

#### Section B. (at high temperatures)

From the literature we find that increasing the pressure or raising the temperature accelerates the process of corrosion. In view of the foregoing, the same experiments were carried out in an autoclave at  $120^\circ\text{C}$ . and 15 lbs. of steam pressure for a period of one hour. To account for changes in volume produced by evaporation, the containers were carefully weighed before the experiment and after and the proper adjustments made. The data and results of these experiments are given in Appendix, Table II. For a graphical representation of the results see Appendix, Fig. II. From the results so obtained it is found that the action taking place under increased pressure and higher temperature is similar to that at room temperature except that it is more vigorous and accelerated. By comparison of Appendix, Figs. I and II, the similarity can readily be seen. Analysis of the solution of sample No. 5 showed it to contain 0.6 gm. zinc per 100 cc. of sample used. The other samples were tested qualitatively and were found to contain zinc, also small amounts of Cu and traces of Fe. The finding of the latter indicates that oxidization took place to a greater extent than at room temperature, which is to be expected.

#### Section C. (in the presence of $\text{NaCl}$ )

According to the data given in Appendix, Table III, it will be noted that the nitrate-nitrogen content was kept constant while the concentration of  $\text{NaCl}$  was varied. In this case the work was carried out in a manner identical with

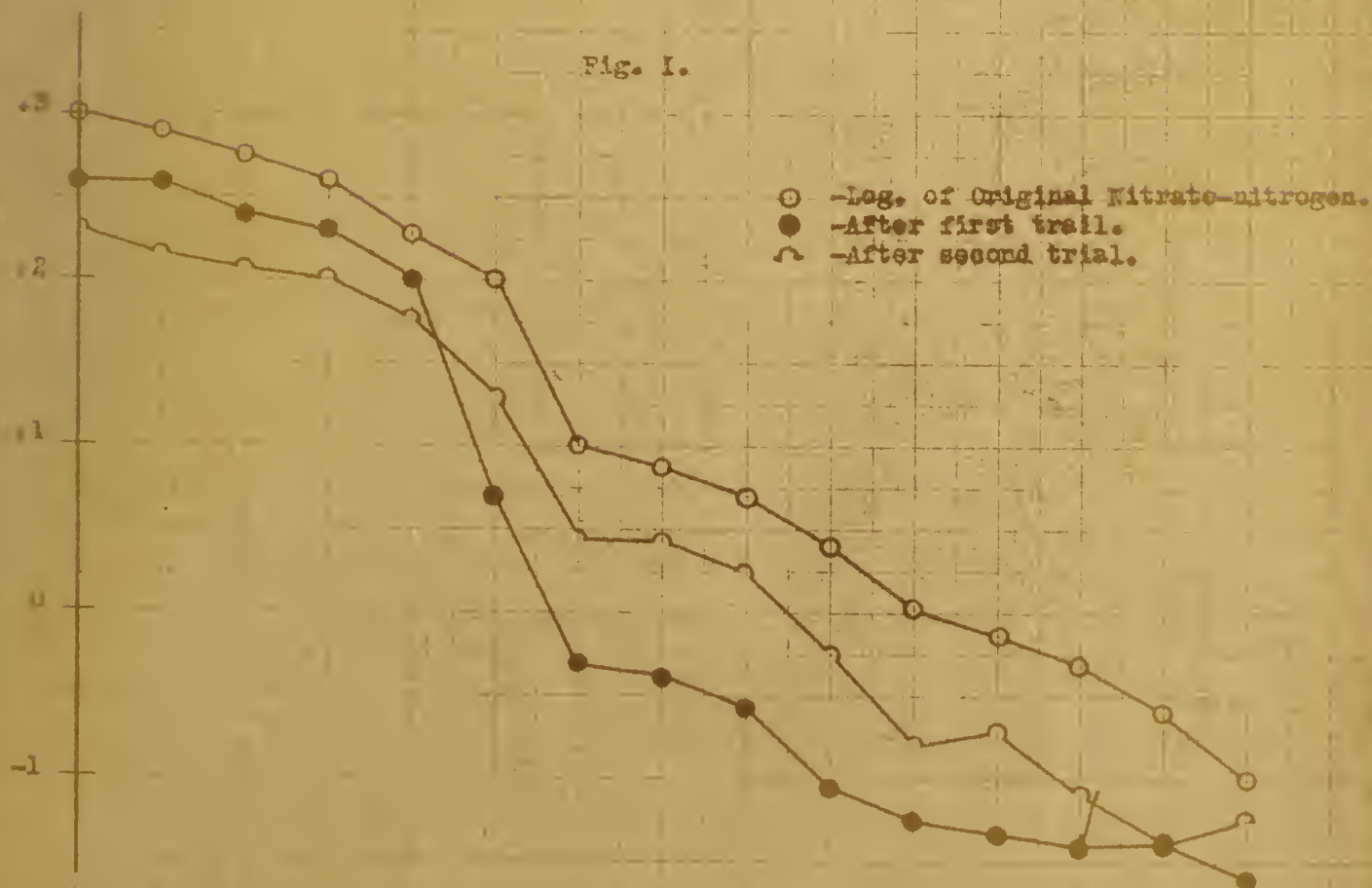


TABLE NO. 1.

P.p.m. Nitrate-Nitrogen (KNO<sub>3</sub> Solution)

No.	First Trial		Second Trial	
	Before	After 30 da.	Before	After 30 da.
1	0	0.024	0	0.12
2	0.10	0.048	0.10	0.18
3	0.25	0.064	0.25	0.16
4	0.50	0.064	0.50	0.20
5	0.75	0.072	0.75	0.32
6	1.00	0.080	1.00	0.38
7	2.50	0.112	2.50	0.70
8	5.00	0.280	5.00	1.80
9	7.50	0.450	7.50	2.80
10	10.00	0.500	10.00	2.80
11	100.00	5.000	100.00	18.00
12	200.00	100.	200.00	60.00
13	400.00	200.	400.00	100.
14	600.00	250.	600.00	120.
15	800.00	400.	800.00	140.
16	1000.00	400.	1000.00	200.

Fig. I.







with that described in Section A, except that agitation was used. Agitation was secured by making a bundle of the tubes and placing them on a shaking apparatus. In this case two trials of 48-hour each were made. The results show no consistency as can be noted from the curves in Appendix, Fig. III.

Section D. (In the presence of NaCl, CaCO<sub>3</sub>, and CO<sub>2</sub>)

The composition of the solutions used with additional data is given in Appendix, Table IV. One liter of the solution was shaken up for a period of 15 hours at room temperature, with 50 gms. of standard brass turnings obtained from the Bureau of Standards. The following analysis was submitted with the sample:

Sheet Brass Sample No. 37

Tin	1.013%	Zinc	26.89%
Lead	0.964%	Iron	0.29%
Copper	70.290%	Nickel	0.52%

The NO<sub>3</sub>, NO<sub>2</sub>, and NH<sub>3</sub> values were obtained before and after the 15-hour interval. These are given in Appendix, Table IV and plotted in Appendix, Fig. IV. It might be mentioned here that the precipitates obtained are of a colloidal nature and invariable were dispersed in the presence of electrolytes as NaCl.

Section E. (In KNO<sub>3</sub>, natural water, and synthetic water).

To explain the use of the particular natural water it might be said that the water furnishing the city supply of Pekin, Illinois, is a good example of a very corrosive water. Numerous meters as well as pumping apparatus parts have been and are being, literally eaten away by their water. The following analysis of the Pekin supply was made January 15, 1919:-





TABLE NO. II.

Autoclave at 154° 1 hr. (200 cc of  $\text{KNO}_3$  sol.)

No.	Original p.p.m. $\text{NO}_3\text{-N}$	After 1st trial p.p.m. $\text{NO}_3\text{-N}$	After 2d trial p.p.m. $\text{NO}_3\text{-N}$
1	1.0	0.40	0.70
2	2.0	0.64	1.30
3	10.0	2.80	6.00
4	20.0	4.40	12.00
5	400.0	80.00	20.00*
6	0.4	0.32	

\* 0.6 gr. Zn per 100 cc sample.

FIG. II

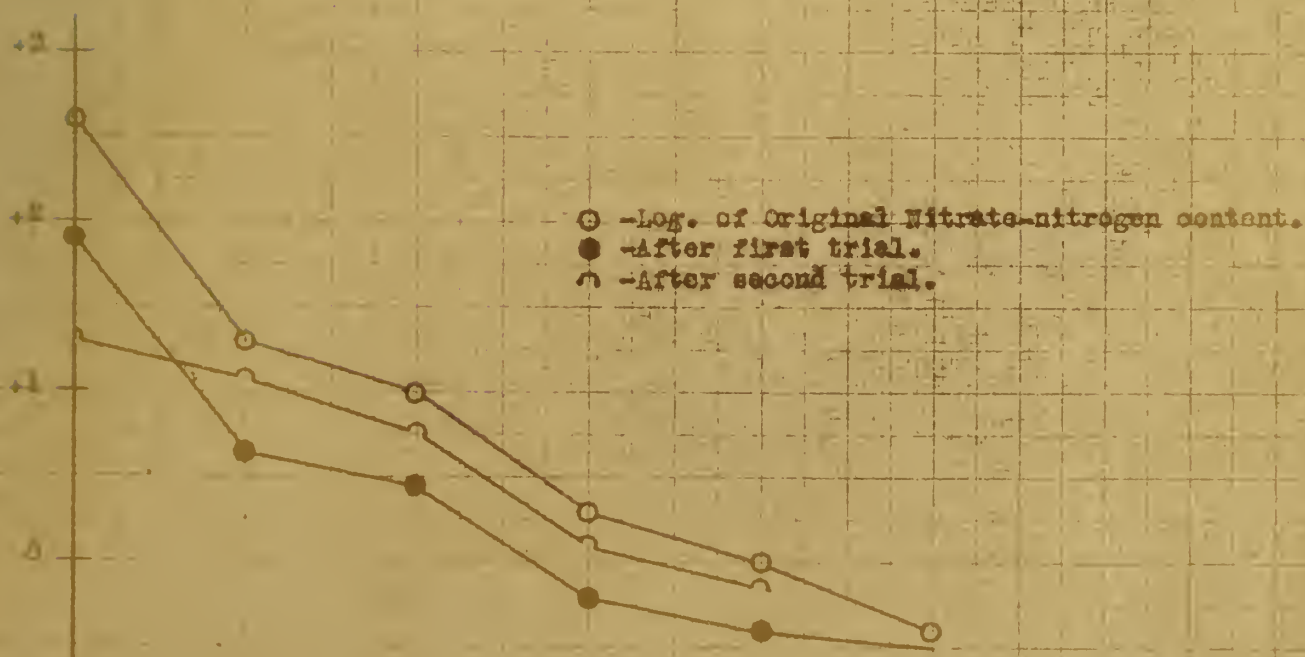




TABLE NO. III.

## P.p.m. Nitrate - Nitrogen

No.	Orig.	After 48 hrs.	2nd Trial	Comp. of Sol.
Blank	0	1.28	0.8	NH <sub>4</sub> - Free H <sub>2</sub> O
1	1400	1280	.800	25 cc - x 25 cc - H <sub>2</sub> O
2	1400	960	1200	25 cc - x 5 cc - y 20 cc - H <sub>2</sub> O
3	1400	960	800	25 cc - x 10 cc - y 15 cc - H <sub>2</sub> O
4	1400	1120	800	25 cc - x 15 cc - y 10 cc - H <sub>2</sub> O
5	1400	1280	800	25 cc - x 20 cc - y 5 cc - H <sub>2</sub> O
6	1400	1120	720	25 cc - x 25 cc - y 0 cc - H <sub>2</sub> O
7	1400	800		25 cc - x 25 cc - y 0 cc - H <sub>2</sub> O
Blank	0	1.44	3.2	50 cc - y

$x = \frac{N}{5} \text{ KNO}_3$        $x = \frac{N}{2.5} \text{ NaCl}$   
 $y = \frac{N}{5} \text{ NaCl}$        $\text{H}_2\text{O} = \text{NH}_4 \text{ Free}$

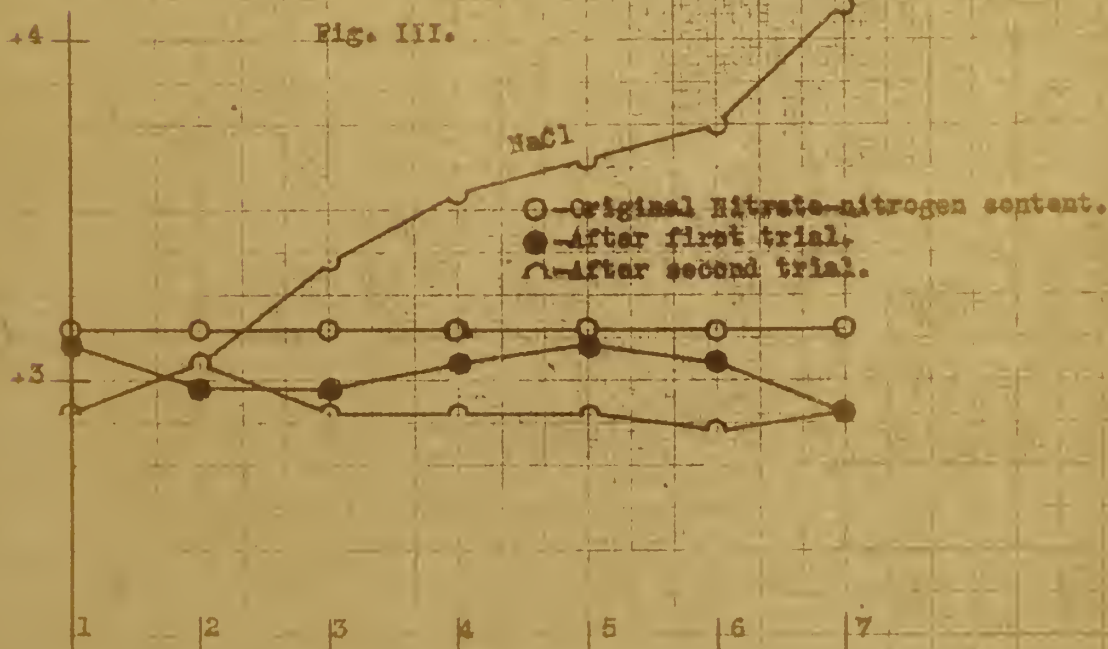




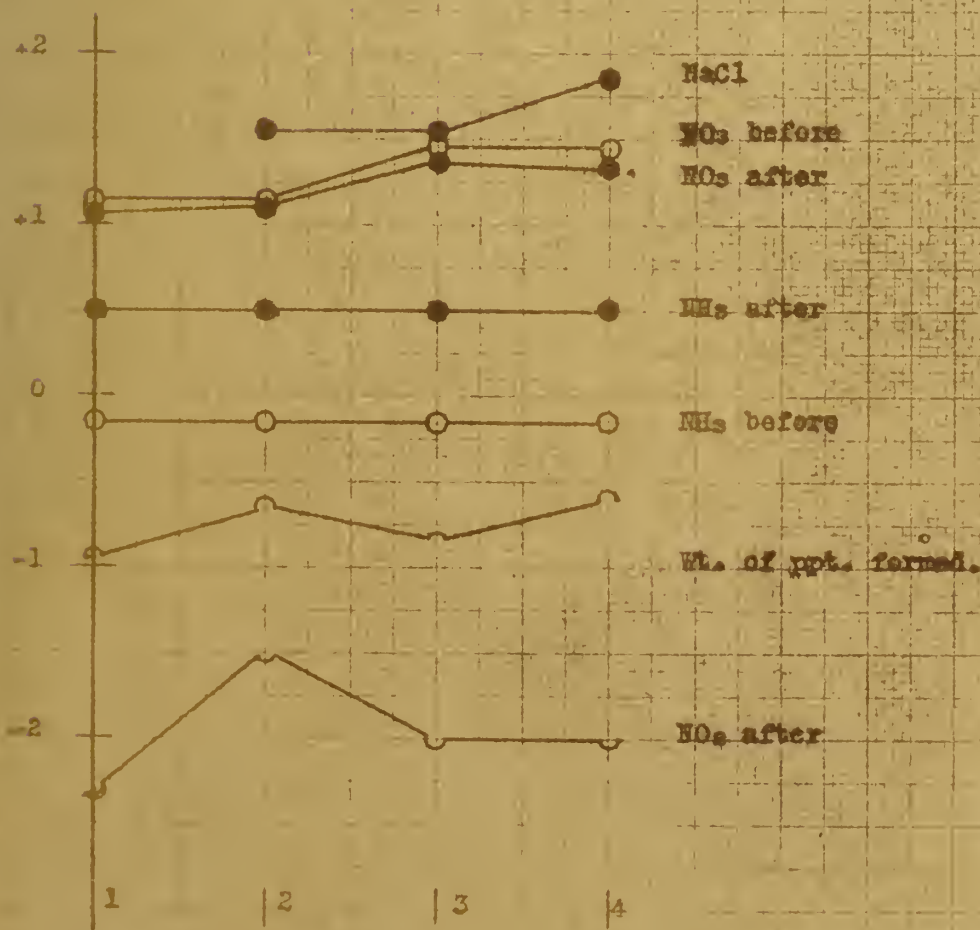


TABLE NO. IV.

P.p.m. Nitrate- Nitrogen

No.	Before		After (15 hrs. shaking)			Comp. of solids in p.p.m.
	P.p.m. NH <sub>3</sub>	p.p.m. NO <sub>3</sub>	P.p.m. NH <sub>3</sub>	p.p.m. NO <sub>2</sub>	p.p.m. NO <sub>3</sub>	
1	0.72	14	3.2	0.005	12	KNO <sub>3</sub> 72.2 CaCO <sub>3</sub> 150
2	0.72	14	3.2	0.030	14	KNO <sub>3</sub> 72.2 CaCO <sub>3</sub> 150. NaCl 22
3	0.72	28	3.2	0.010	24	KNO <sub>3</sub> 144.4 CaCO <sub>3</sub> 150. NaCl 22
4	0.72	28	3.2	0.010	22	KNO <sub>3</sub> 144.4 CaCO <sub>3</sub> 150 NaCl 124

Fig. IV.





Pekin, City Supply.

Lab. No. 40586.

<u>Ions</u>	<u>p.p.m.</u>	<u>Ions</u>	<u>p.p.m.</u>	<u>Hyp. comb.</u>	<u>p.p.m.</u>
Na	25.44	Fe <sub>2</sub> O <sub>3</sub>	0	NaNO <sub>3</sub>	48.46
NH <sub>4</sub>	0.	Al <sub>2</sub> O <sub>3</sub>	2.0	NaCl	31.28
Mg	36.74	SiO <sub>2</sub>	20.2	MgCl <sub>2</sub>	22.86
Ca	84.61	Non.vol.	1.8	MgSO <sub>4</sub>	67.41
NO <sub>2</sub>	0.	Alk.	264.	MgCO <sub>3</sub>	59.70
NO <sub>3</sub>	35.43	Res.	500.	CaCO <sub>3</sub>	211.28
Cl	36.00			Al <sub>2</sub> O <sub>3</sub>	2.00
SO <sub>4</sub>	53.84	<u>Gases</u>	<u>p.p.m.</u>	SiO <sub>2</sub>	20.2
CO <sub>3</sub>	158.40	CO <sub>2</sub>	20.00	Non.vol.	1.8
		H <sub>2</sub> S	0.25	Total	464.99

Due to the fact that at this time we were interested in the nitrate content of the solutions that were used, a synthetic water was made up corresponding to the analysis of the Pekin supply, also a KNO<sub>3</sub> solution corresponding to the nitrate content of the Pekin water. To 1500 c.c. of each of these three solutions were added 150 gr. of yellow brass turnings. The three containers were placed on a shaking machine and agitated in that manner for a period of fifteen hours. The data and results of the experiment are tabulated in Table V., and represented graphically in Appendix, Fig. V. The Zn in the solution was<sup>24</sup> determined from a representative sample according to the method of Ward. In this experiment the dispersion of the colloid formation in the presence of electrolytes was so striking that photographs of the same were made and are shown in Plate II.

### SUMMARY

#### Section F.

In consideration of this experimental work it is shown that the nitrate-ion is a source of oxygen in the corrosion of brass, in that a consistent reduction of the nitrate-nitrogen contents of the solutions in contact with the brass was obtained. The results obtained by trying to investigate this nitrate reduction in the presence of other salts were too diversified to draw any conclusions from.



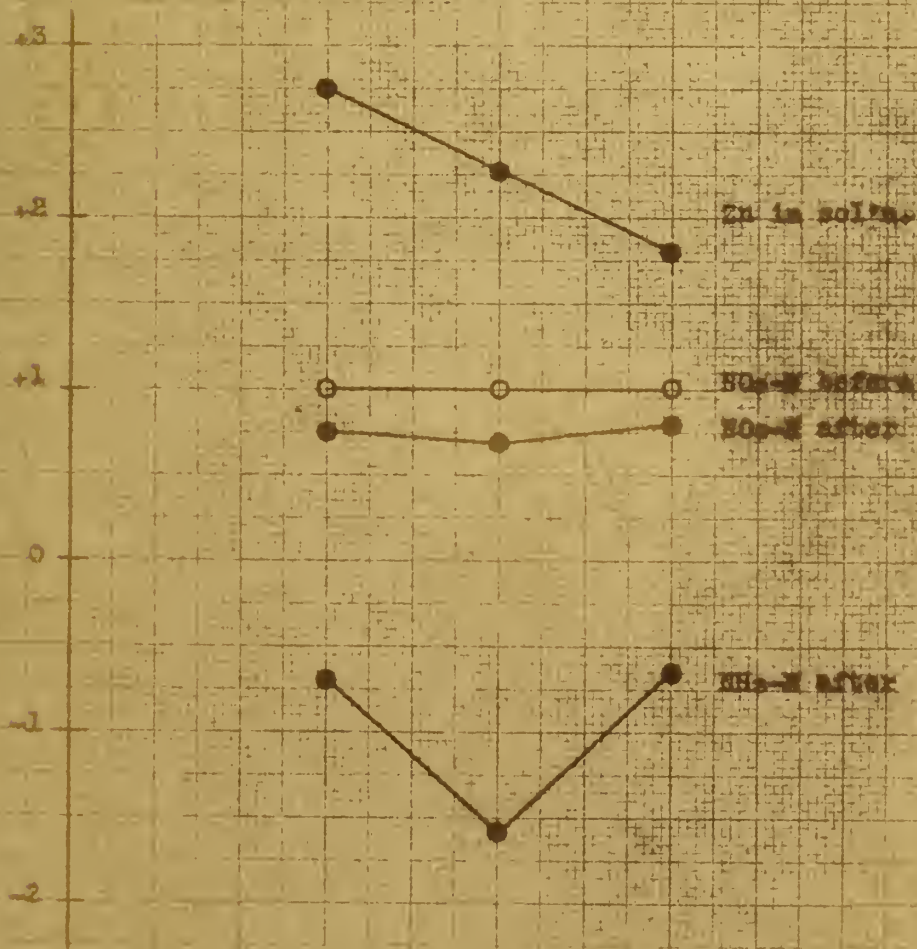


TABLE NO. V.

Etching, 150 gr. common yellow brass with 1500 cc soln. for 15 hours.

No.	P.p.m. $\text{HNO}_3$ - Nitrogen		P.p.m. $\text{NH}_3$ - N		P.p.m. Zn	Comp. of soln.
	Before	After	Before	After		
1	10.0	5.9	0	0.200	572	$\text{HNO}_3$
2	10.0	5.1	0	0.048	179	Nat. water
3	10.0	6.9	0	0.245	65	Syn. water

Fig. V.







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### ACKNOWLEDGMENT.

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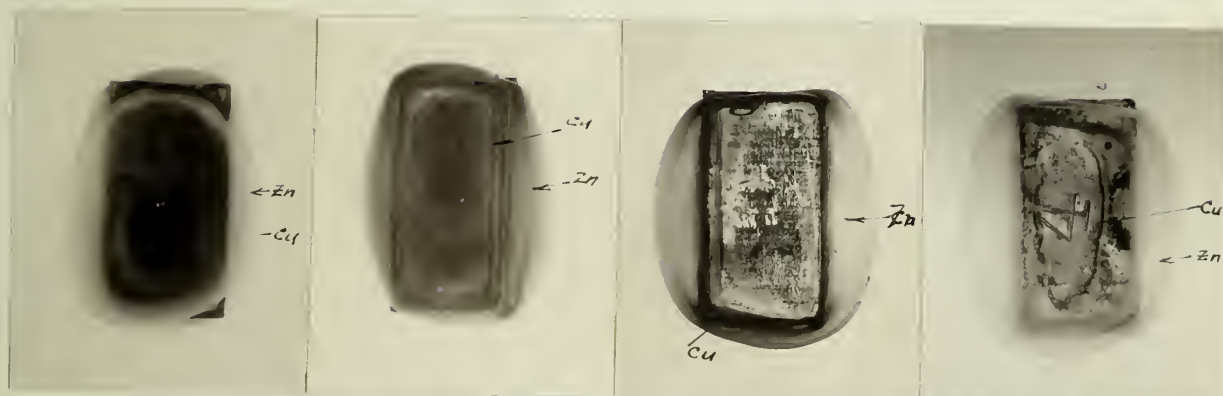
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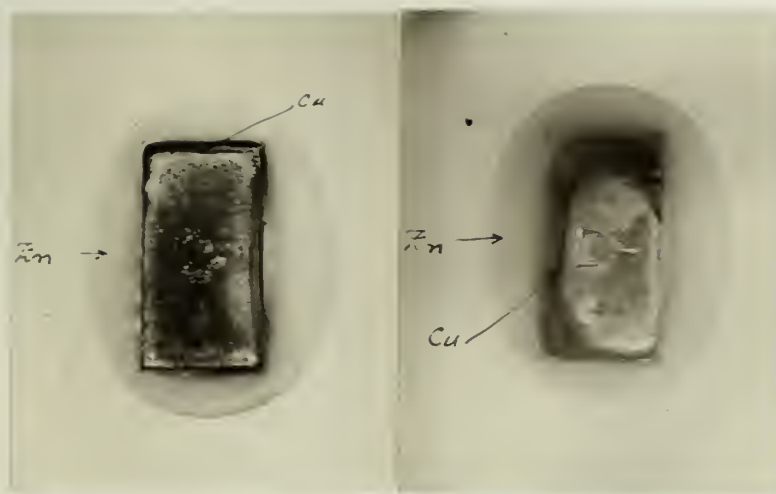


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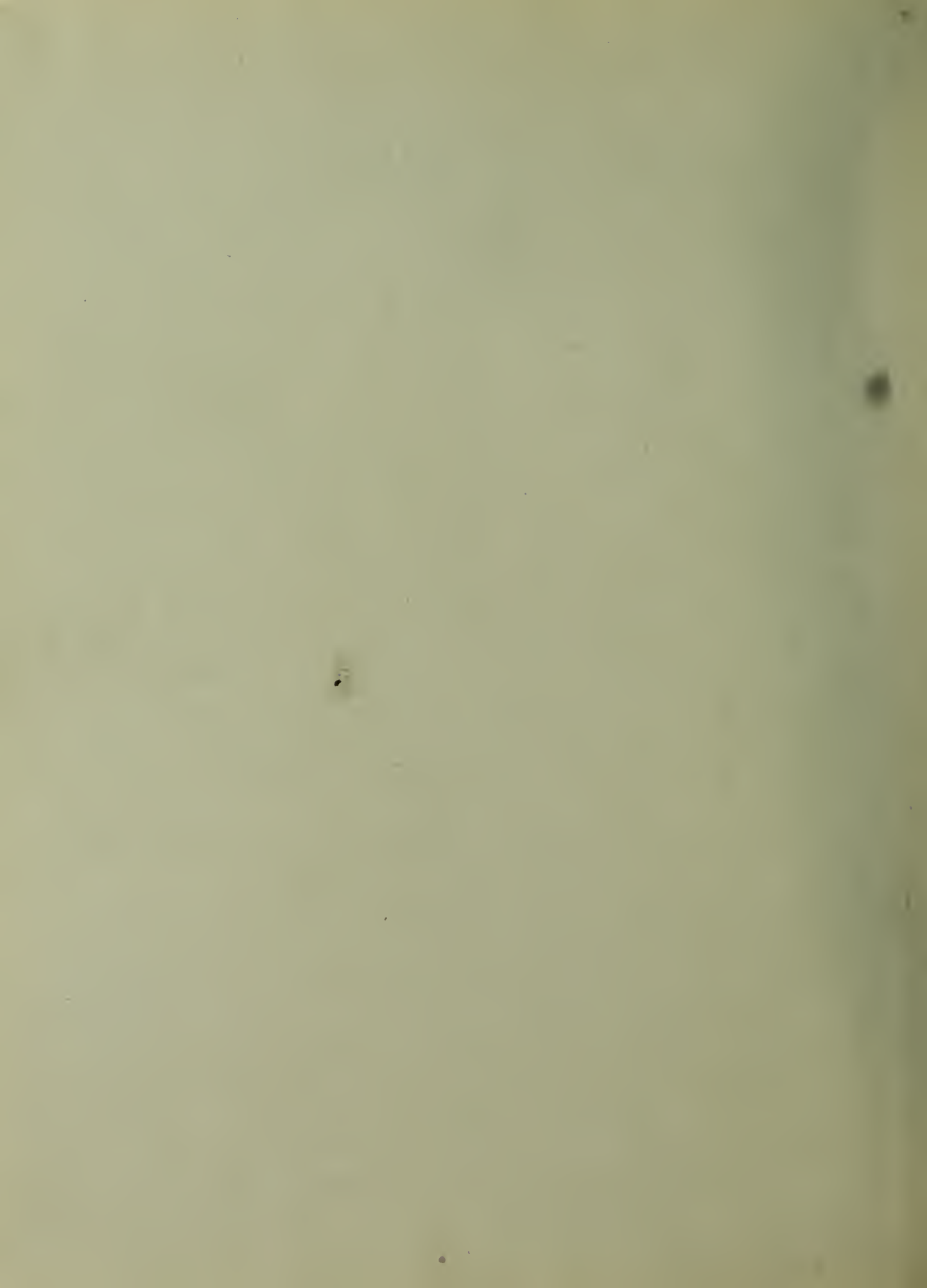
Plate II.







Plate III.





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